IFW
AF

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

IN RE APPLICATION OF:	BARGHOORN ET AL.	MAIL STOP:	APPEAL BRIEF
SERIAL NO.	09/936,353	CONFIRMATION NO.:	4186
FILED:	SEPTEMBER 11, 2001	GROUP ART UNIT:	1713
		EXAMINER:	PETER D. MULCAHY

FOR: STYRENE COPOLYMERS WITH IMPROVED CHEMICAL RESISTANCE
TO: HON. COMMISSIONER OF PATENTS AND TRADEMARKS

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to Commissioner of Patents and Trademarks, Alexandria, Va 22313-1450, on: September 15, 2004
Date of Deposit
Herbert B Keil
Person Making Deposit
/Herbert B Keil
Signature
September 15, 2004
Date of Signature

Sir:

1. ☐ NOTICE OF APPEAL: Applicant hereby appeals to the Board of Appeals from the decision dated -/-, of the Primary Examiner finally rejecting Claims -/-.
2. ☒ Applicants hereby petition for a -/- month extension of time under 37 C.F.R. §1.136. Applicants request entry of their timely reply for purposes of appeal.
   ☐ A check to cover the fee of -/- is enclosed.
   ☐ A petition for a -/- month extension of time including the requisite fee of -/- has been filed along with the amendment under 37 C.F.R. §1.116 dated -/-.
3. ☒ BRIEF ON APPEAL in this application is transmitted herewith.
4. ☐ An oral Hearing is requested
   ☐ The Oral Hearing fee of -/- is enclosed.
5. ☒ Fee *$330.00*
   ☒ Enclosed.
   ☐ Not required (Fee paid in prior appeal).
   ☐ Charge to Deposit Account No. 11.0345.
6. ☒ The Commissioner is hereby authorized to charge any fee which may be further required, or credit any over payment to Deposit Account No. 11.0345. A duplicate copy of this sheet is attached.

Respectfully submitted,
KEIL & WEINKAUF
/Herbert B Keil
Herbert B. Keil
Reg. No. 18,967

1350 Connecticut Ave, N.W.
Washington, D.C. 20036
(202) 659-0100

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

IN RE APPLICATION		MAIL STOP:	APPEAL BRIEF
OF:	BARGHOORN ET AL.	CONFIRMATION NO.:	4186
SERIAL NO.	09/936,353	GROUP ART UNIT:	1713
FILED:	SEPTEMBER 11, 2001	EXAMINER:	PETER D. MULCAHY

FOR: STYRENE COPOLYMERS WITH IMPROVED CHEMICAL RESISTANCE

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to Commissioner of Patents and Trademarks, Alexandria, Va 22313-1450, on:

September 15, 2004
Date of Deposit

Herbert B. Keil
Person Making Deposit

Herbert B Keil
Signature

September 15, 2004
Date of Signature

Honorable Commissioner
for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

BRIEF ON APPEAL UNDER 37 C.F.R. §1.192

Sir:

This is an appeal from the Examiner's final rejection of Claims 9 to 12 and 14 to 21, dated April 07, 2004. Claims 9, 10, 14 to 17 and 21 are currently pending.

REAL PARTY IN INTEREST:

The real party in interest is BASF Aktiengesellschaft, 67056 Ludwigshafen, Germany.

RELATED APPEALS AND INTERFERENCES:

To the best of the undersigned's knowledge, there are no related appeals or interferences within the meaning of 37 C.F.R. §1.192(c)(2).

STATUS OF THE CLAIMS:

The claims on appeal before the Board of Patent Appeals and In-

terferences are Claims 9, 10, 14 to 17 and 21. A copy of these claims is found in the attached Appendix.

STATUS OF THE AMENDMENTS:

Claim 9, 14 and 15 were amended, and Claims 11, 12, 18, 19 and 20 were canceled in reply to the final action (*Reply dated June 25, 2004, Paper No. 8*). Entry and consideration of the amendment was acknowledged by the Examiner in his advisory action dated July 19, 2004, in the section pertaining to the status of the claims. No further amendments have been filed in this application after final rejection.

SUMMARY OF THE INVENTION:

Appellants' invention relates to a method improving the chemicals resistance, reducing the swelling, and improving the stress-cracking resistance of styrene copolymers which comprises adding to the copolymer an effective amount of mica[1]. The method which is defined in appellants' Claim 9 further requires that the mica be added to a particular styrene copolymer constituent to obtain the following composition[2]:

A: from 20 to 100% by weight, based on the entirety of components A + B, of a hard component made from one or more copolymers of styrene and/or α-methylstyrene with acrylonitrile, the proportion of acrylonitrile being from 10 to less than 28% by weight,

B: from 0 to 80% by weight, based on the entirety of components A + B, of at least one graft copolymer B made from

  B1: from 10 to 90% by weight of at least one elastomeric particulate graft base with a glass transition temperature below 0°C, and

  B2: from 10 to 90% by weight of at least one graft made from polystyrene or from a copolymer of styrene and/or α-methylstyrene with acrylonitrile, the proportion of acrylonitrile being from 10 to less than 28% by weight,

where components A + B constitute from 10 to 100 parts by weight, based on the total weight of the components used, and

---

1) Claim 21.

2) Appellants' Claim 15 is limited as concerns the amounts of the constituents in the same manner as Claim 9, and Claims 10 and 14, 16 and 17 incorporate the respective limitations by reference to Claim 9 or Claim 15.

C: from 0.05 to 5 parts by weight, based on the total weight of the components used, of the mica,

D: from 0 to 90 parts by weight, based on the total weight of the components used, of at least one polycarbonate, and

E: from 0 to 20 parts by weight, based on the total weight of the components used, of other conventional auxiliaries and fillers.

The effects which result from the incorporation of the respective amounts of mica into the styrene copolymers are addressed on page 1, indicated lines 28 to 34, of the application, and are illustrated by the data compiled in Table 5, page 20, of the application.

ISSUE(S) PRESENTED:

I) Whether the Examiner erred finding that the subject matter of appellants' Claims 9, 10, 14 to 17 and 21 is unpatentable under 35 U.S.C. §103(a) in light of the teaching of ***Zilg et al.*** **(US 6,197,849)**.

II) Whether the Examiner erred finding that the subject matter of appellants' Claims 9, 10, 14 to 17 and 21 is unpatentable under 35 U.S.C. §103(a) in light of the teaching of ***Hilti et al.*** **(US 5,814,688)**.

GROUPING OF THE CLAIMS:

For the issue(s) above Claims 10 and 14 to 17 stand and fall with Claim 1, and Claim 21 stands alone.

A R G U M E N T S

I.a) The Examiner erred finding that the subject matter of appellants' Claims 9, 10 and 14 to 17 was *prima facie* obvious under 35 U.S.C. §103(a) in light of the teaching of ***Zilg et al.*** **(US 6,197,849)**.

The teaching of ***Zilg et al.*** relates to organophilic phyllosilicates which are obtained by treating a naturally occurring phyllosilicate with at least one salt of a quaternary or other cyclic amidine compound, and to the use of such organophilic phyllosilicates in molding materials[3]. According to ***Zilg et al.*** the organophilic, cf. treated, phyllosilicates are particularly useful as a filler material

3) Inter alia, col. 1, indicated lines 3 to 8, and 37 to 64, of ***US 6,197,849***.

because they exhibit an excellent dispersibility and interfacial adhesion in molding materials due to the presence of the embedded salt(s)[4]. With regard to phyllosilicates which are suitable for preparing the organophilic phyllosilicates, ***Zilg et al.*** mention[5]

> *in particular naturally occurring or synthetic smectite clay minerals, in particular montmorillonite, saponite, beidelite, nontronite, hectorite, sauconite and stevensite, and also bentonite, vermiculite and halloysite.*

As concerns the molding materials in which the organophilic phyllosilicates are to be used as fillers, ***Zilg et al.*** refer to thermoplastic as well as thermosetting polymer systems and to rubbers[6], listing a variety of thermoplastic polymers and rubbers[7] as well as thermosetting polymer systems[8], and mentioning as particularly preferred the combination of the organophilic phyllosilicate(s) with polyurethanes[9].

The Examiner takes the position that appellants' invention was *prima facie* obvious because ***Zilg et al.*** show mica[10] and show the constituents of the styrene-acrylonitrile copolymer defined in appellants' claims[11].

Appellants find no mention or showing of mica in the teaching of ***Zilg et al.*** The phyllosilicates encompass numerous groups of minerals which vary broadly in structure and in properties[12]. The smectite clay minerals which are generically mentioned by ***Zilg et al.*** constitute one subgroup of phyllosilicates. One of the characteristics of smectite clay minerals is that they have an expanding lattice[13].

---

4) Col. 1, indicated lines 9 to 18, in conjunction with col. 1, indicated lines 59 to 64, of ***US 6,197,849***.

5) Col. 2, indicated lines 38 to 43, of ***US 6,197,849***.

6) Col. 5, indicated lines 23 to 28, of ***US 6,197,849***.

7) Col. 5, indicated lines 40 to 65, of ***US 6,197,849***. In this context, styrene-acrylonitrile copolymers are mentioned in indicated lines 49 and 50, and indicated lines 52 and 53 provide that the thermoplastic polymers may also be employed in mixture with rubbers.

8) Col. 5, indicated line 66, to col. 7, indicated line 62, of ***US 6,197,849***.

9) Col. 7, indicated line 63, to col. 10, indicated line 5, of ***US 6,197,849***.

10) Advisory action dated July 19, 2004 (Paper No. 09), page 2.

11) Office action dated October 03, 2003 (Paper No. 05), page 2, lines 16 to 27, Office action dated April 07, 2004 (Paper No. 07), page 2, line 26, to page 3, line 5.

12) For example, ***Ullmann's*** *Encyclopedia of Industrial Chemistry*, 5th Ed., VCH Verlagsgesellschaft mbH, Weinheim (Germany), Vol. A7 (1986), page 110, left column, subsections II.A to II.C, and page 112, right column, first para (*copy enclosed*); and ***Ullmann's*** *Encyclopedia of Industrial Chemistry*, 5th Ed., VCH Verlagsgesellschaft mbH, Weinheim (Germany), Vol. A23 (1993), page 669, Table 4 (*copy enclosed*).

13) ***Ullmann's*** A7, page 131, para 2 of subsection 4.2. (*copy enclosed*).

Mica minerals also constitute a subgroup of phyllosilicates. However, in contrast to the lattice of smectite minerals the lattice of micas is non-expanding[14]. The Examiner's position that ***Zilg et al.*** show mica is therefore deemed to be in error.

Appellants' Claim 9 refers to a specific styrene-acrylonitrile copolymer which is composed of

A) from 20 to 100% by weight of a hard component (A) made from one or more copolymers of styrene and/or α-methylstyrene with acrylonitrile, wherein the proportion of acrylonitrile is from 10 to less than 28% by weight, and

B) from 0 to 80% by weight of at least one graft copolymer (B) made from

   B1) from 10 to 90% by weight of at least one elastomeric particulate graft base with a glass transition temperature below 0°C, and

   B2) from 10 to 90% by weight of at least one graft made from polystyrene or from a copolymer of styrene and/or α-methylstyrene with acrylonitrile, wherein the proportion of acrylonitrile is from 10 to less than 28% by weight,

wherein the weight percentages of (A) and (B) are based on the total weight of (A + B).

In the enumeration of classes of thermoplastic polymers, ***Zilg et al.*** *inter alia* refer to styrene-acrylonitrile copolymers in general and ***Zilg et al.*** also mention that thermoplastic polymers may be employed in mixture with rubbers[15]. However, ***Zilg et al.*** provide no information whatsoever with regard to the proportion of styrene to acrylonitrile in such styrene-acrylonitrile copolymers or with regard to grafted rubbers and particularities of the graft shell thereof. The Examiner's position that ***Zilg et al.*** show the constituents of appellants' styrene-acrylonitrile copolymer is therefore not deemed to be well taken.

The Examiner further argues that appellants' invention was *prima facie* obvious because case law has established that it is prima facie obvious to select ingredients from a list and have them function in an expected manner[16].

---

14) ***Ullmann's*** A7, page 112, para. 1 of the right hand column (*copy enclosed*).

15) See ftn. (7) on page 4 of this paper.

16) Paper No. 05, page 2, lines 16 to 27; Paper No. 07, page 2, line 26, to page 3, line 5.

The Examiner's argument is not deemed to support a finding of obviousness under Section 103(a) where appellants' invention and the teaching of ***Zilg et al.*** is concerned. On the one hand, neither mica nor the specific styrene-acrylonitrile copolymer defined in appellants' claims can be selected from a list provided by the teaching of ***Zilg et al.*** On the other hand, case law has also established that obviousness under Section 103(a) requires more than the mere fact that a claimed species or subgenus is encompassed by a generic teaching of the prior art[17)]. Regardless of the type of disclosure, cf. the generic disclosure of one prior art reference or the disclosure which is provided by a combination of prior art references, the prior art must contain something which would motivate a person of ordinary skill in the art to make the particular selection which is necessary to arrive at the claimed invention[18)]. The teaching of ***Zilg et al.*** does not address a combination of phyllosilicates and molding materials. Rather, ***Zilg et al.***'s teaching deals with organophilic phyllosilicates, cf. phyllosilicates which are modified by way of ion exchange to contain at least one salt of a quaternary or other cyclic amidine compound. Not only the organophilic phyllosilicates but also the phyllosilicates which are employed in the preparation of the organophilic phyllosilicates according to ***Zilg et al.***'s teaching differ from mica. The teaching of ***Zilg et al.*** therefore cannot be deemed to motivate a person of ordinary skill in the art to select mica and combine it with any molding material.

Moreover, since the teaching of ***Zilg et al.*** is not concerned with the effect of *unmodified* phyllosilicates on molding materials, the teaching is unsuited to raise any expectation with regard to the effect which results from such a combination. The Examiner's position that the "selected" ingredients act in the context of appellants' invention "in an expected manner" is accordingly not deemed to be well taken where appellants' invention and the teaching of ***Zilg et al.*** is concerned.

Appellants' Claim 9 relates to a method which *inter alia* provides for an improvement of the chemicals resistance and a reduction of the

---

17) In re Baird, 16 F.3d 380, 382, 29 USPQ2d 1550, 1552 (CAFC 1994); In re Jones, 958 F.2d 347, 350, 21 USPQ2d 1941, 1943 (CAFC 1992); In re Deuel, 51 F.3d 1552, 1559, 34 USPQ2d 1210, 1215 (CAFC 1995).

18) In re Vaeck, 947 F.2d 488, 493, 20 USPQ2d 1438, 1442 (CAFC 1991); In re Dow Chemical Co., 837 F.2d 469, 473, 5 USPQ2d 1529, 1531 (CAFC 1988); Hodosh v. Block Drug Co., 786 F.2d 1136, 1143 n.5, 229 USPQ 182, 187 n.5 (CAFC 1986).

swelling of the specific styrene-acrylonitrile copolymer defined in the claim. It is well settled that not only the materials which are used and the nature of the process which is employed but also the specific result which is achieved must be considered when determining whether a claimed method is obvious within the meaning of Section 103[19)20)]. Since the teaching of ***Zilg et al.*** does not address any effects which arise from a combination of an *unmodified* phyllosilicate and thermoplastic materials, it clearly provides nothing which raises the expectation that the combination of the specific styrene-acrylonitrile copolymer defined in appellants' claim and the requisite amounts of mica results in the increased chemicals resistance and in the reduced swelling of the material which is shown in the experiments described in the application.

The Examiner asserts that it is reasonable to presume that the prior art compositions exhibit the same properties as addressed in appellants' method and inherent in appellants' composition[21)]. The Examiner's position is deemed to be in error because the teaching of ***Zilg et al.*** does not relate to polymer compositions which comprise an *unmodified* phyllosilicate or, more particularly, mica.

Moreover, the question under Section 103 is whether the claimed invention was prima facie obvious to a person of ordinary skill <u>at the time the invention was made</u>. It is well settled that obviousness cannot be predicated on what is not known at the time an invention is made, even if the inherency of a certain feature is later established[22)]. It constitutes hindsight when one of ordinary skill in the art is imbued with the knowledge of the invention, when the prior art reference fails to convey or suggest that knowledge[23)]. When applying 35 U.S.C. §103, the prior art reference or references must be viewed without the benefit of impermissible hindsight vision afforded by the claimed invention[24)].

19) <u>In re Dillon</u>, 919 F.2d 688, 695, 16 USPQ2d 1897, 1903 (CAFC 1990) (*en banc*), *cert. denied*, 500 U.S. 904 (1991).

20) Correspondingly, where a composition of matter such as defined in appellants' Claims 15 and 16 is concerned, the invention as a whole which is referenced in Section 103 encompasses the properties which are inherent in the combination defined in the claim. <u>In re Antonie</u>, 559 F.2d 618, 620, 195 USPQ 6, 8 (CCPA 1977).

21) Paper No. 07, page 3, lines 3 to 16.

22) <u>In re Rijckaert</u>, 9 F.2d 1531, 28 USPQ2d 1955 (CAFC 1993); <u>In re Adams</u>, 356 F.2d 998, 148 USPQ 742 (CCPA 1966).

23) <u>Gore & Assocs., Inc. v. Garlock, Inc.</u>, 721 F.2d 1540, 230 USPQ 303 (CAFC 1983).

24) <u>Hodosh v. Block Drug Co., Inc.</u>, 786 F.2d 1136, 1143 n.5, 229 USPQ 182, 187 n.5 (CAFC 1986).

I.b) <u>The Examiner erred finding that the subject matter of appellants' Claim 21 was *prima facie* obvious under 35 U.S.C. §103(a) in light of the teaching of ***Zilg et al.*** **(US 6,197,849)**</u>.

Appellants' Claim 21 relates to a method for improving the chemicals resistance, reducing the swelling, and improving the stress-cracking resistance of styrene copolymers, which comprises adding to said copolymers an effective amount of mica.

The Examiner takes the position that the teaching of ***Zilg et al.*** renders the process step of adding mica to a styrene copolymer prima facie obvious[25)].

However, as already addressed in the foregoing, when determining whether a claimed *method* is obvious within the meaning of Section 103, it is not only the materials which are used and the nature of the process which is employed which have to be considered. The determination also has to take the particular result into account which is achieved by the method[26)]. As also already addressed in the foregoing, ***Zilg et al.*** are not concerned with *unmodified* phyllosilicates in general, or with mica in particular. As such, the teaching of ***Zilg et al.*** is not deemed to render the addition of mica to a styrene copolymer *prima facie* obvious. Correspondingly, the teaching of ***Zilg et al.*** cannot suggest or imply an effect which results when appropriate amounts of mica are incorporated into a styrene copolymer. Accordingly, the teaching of ***Zilg et al.*** cannot be deemed to render a method obvious within the meaning of Section 103(a) in which the chemicals resistance is improved, the swelling is reduced, and the stress-cracking resistance is improved by adding effective amounts of mica to a styrene copolymer.

II) <u>The Examiner erred finding that the subject matter of appellants' Claims 9, 10, 14 to 17 and 21 was *prima facie* obvious under 35 U.S.C. §103(a) in light of the teaching of ***Hilti et al.*** **(US 5,814,688)**</u>.

The teaching of ***Hilti et al.*** relates to polar, adsorptive inorganic or organic materials which are impregnated with polar antistatic agents comprising (b_1) at least one polar organic compound, and (b_2) a salt of an inorganic protic acid which is solvated or complexed in the polar organic compound, and to the use of the impregnated

25) Paper No. 07, page 3, lines 17 to 22.

26) See ftn. (19) on page 7 of this paper.

materials in polymers[27]. According to ***Hilti et al.***, the impregnated inorganic or organic materials are particularly useful as antistatic agents because they form, when incorporated into the polymer, electrically conducting tracks which allow static charges to drain away[28]. The inorganic or organic materials mentioned by ***Hilti et al.*** as suitable for the preparation of the antistatic agents include

> *... naturally occurring mineral flours, such as calcite, talc, kaolin, diatomaceous earth, montmorillonite[29)] or attapulgite[30)] ... phyllosilicates, such as sepiolite[30)] or bentonite[29)], highly disperse silicic acids, synthetic, highly absorbent silicic acid, silica gels, molecular sieve zeolites, pumice, crushed brick or porous glass.*[31]
>
> *... synthetic porous polymers, for example urea-formaldehyde polycondensates (Pergopak), ...*[32]
>
> *... granular or fibrous, naturally occurring organic materials, such as comminuted wood or plant residues, or processed natural fibres ... preferred ... cellulose fibres, such as cotton, bast, kapok, jute, ramie, flax and hemp ... wool or silk fibres.*[33]
>
> *... synthetic polymer fibres ...*[34]

As polymers into which the antistatic agents which are obtained from the inorganic or organic materials may be incorporated ***Hilti et al.*** enumerate twenty-eight groups, including blends[35], and ***Hilti et al.*** mention that the antistatic agents have virtually no effect on the stability properties of the polymers[36].

The Examiner argues -similar to the position taken with regard to the teaching of ***Zilg et al.***-

- that appellants' invention was *prima facie* obvious because ***Hilti***

---

27) Inter alia, col. 1, indicated lines 3 to 20, and col. 2, indicated lines 16 to 27, of ***US 5,814,688***.

28) Col. 2, indicated lines 16 to 23, and indicated lines 40 to 45, of ***US 5,184,688***.

29) phyllosilicate of the smectite group, ie. ***Ullmann's*** ..., vol. A7, page 110, and vol. A23, page 662.

30) phyllosilicate of the hormite group, ie. ***Ullmann's*** ..., vol. A7, pages 110 and 112.

31) Col. 6, indicated lines 26 to 32, of ***US 5,184,688***.

32) Col. 7, indicated lines 1 to 4, of ***US 5,184,688***.

33) Col. 7, indicated lines 9 to 22, of ***US 5,184,688***.

34) Col. 7, indicated lines 23 to 39, of ***US 5,184,688***.

35) Col. 2, indicated line 64, to col. 5, indicated line 60, of ***US 5,814,688***. In this context, styrene-acrylonitrile copolymers and blends thereof are mentioned in col. 4, indicated lines 1 to 12.

36) Col. 2, indicated lines

et al. show mica[37] and show the constituents of the styrene-acrylonitrile copolymer defined in appellants' claims[38];

- that appellants' invention was *prima facie* obvious because case law has established that it is prima facie obvious to select ingredients from a list and have them function in an expected manner[39];
- that it is reasonable to presume that the compositions taught by ***Hilti et al.*** exhibit the properties which result in accordance with appellants' method and which are inherent in appellants' composition[40]; and
- that the teaching of ***Hilti et al.*** renders the process step of adding mica to a styrene copolymer prima facie obvious[41].

However, the teaching of ***Hilti et al.*** is comparable to the teaching of ***Zilg et al.*** in that -like ***Zilg et al.***-

- ***Hilti et al.*** merely mention phyllosilicates which differ from mica in structure and in properties;
- ***Hilti et al.*** merely mention the phyllosilicates as a group of starting materials for the preparation of the antistatic agents;
- ***Hilti et al.*** merely provide a laundry list of generic groups of polymeric materials into which the antistatic agents can be incorporated; and
- ***Hilti et al.*** fail to address the incorporation of any unmodified phyllosilicate into any polymer, and correspondingly fail to suggest an effect which is achieved when an unmodified phyllosilicate is incorporated into a polymer.

Appellants' arguments in sections (I.a) and (I.b) of this brief are therefore equally applicable where the Examiner's rejection under Section 103(a) based on the teaching of ***Hilti et al.*** is concerned.

CONCLUSION

For the foregoing reasons, appellants respectfully urge that the

---

37) Paper No. 09, page 2.

38) Paper No. 05, page 2, lines 16 to 27; Paper No. 07, page 2, line 26, to page 3, line 5.

39) Paper No. 05, page 2, lines 16 to 27; Paper No. 07, page 2, line 26, to page 3, line 5.

40) Paper No. 07, page 3, lines 3 to 16.

41) Paper No. 07, page 3, lines 17 to 22.

Examiner erred finding that appellants' invention defined in Claims 9, 10, 14 to 17 and 21 was obvious within the meaning of Section 103(a) in light of the teaching of ***Zilg et al.*** and in light of the teaching of ***Hilti et al.*** It is therefore respectfully requested that the Examiner's respective rejections of appellants' Claims 9, 10, 14 to 17 and 21 under 35 U.S.C. §103(a) be reversed.

Please charge any shortage in fees due in connection with the filing of this paper, including Extension of Time fees, to Deposit Account No. 11.0345. Please credit any excess fees to such deposit account.

Respectfully submitted,
KEIL & WEINKAUF

Herbert B Keil

Herbert B. Keil
Reg. No. 18,967

1350 Connecticut Ave, N.W.
Washington, D.C. 20036
(202) 659-0100

Encl.: THE CLAIMS ON APPEAL (Appendix II)
***Ullmann's** Encyclopedia of Industrial Chemistry*, 5th Ed., VCH Verlagsgesellschaft mbH, Weinheim (Germany),
- Vol. A7 (1986), pp. 109-113, pp. 126-133
- Vol. A23 (1993), pp. 661-674

HBK/BAS

APPENDIX I:

THE CLAIMS ON APPEAL:

9. A method for improving the chemicals resistance, reducing the swelling, and improving the stress-cracking resistance of styrene-acrylonitrile copolymers having a proportion of acrylonitrile of less than 28% by weight, comprising the step of adding phyllosilicates to said styrene-acrylonitrile copolymers, wherein the styrene-acrylonitrile copolymers have been built up from components A, C, and, where appropriate, B, D, and E, using:

   a: as component A, from 20 to 100% by weight, based on the entirety of components A + B, of a hard component made from one or more copolymers of styrene and/or α-methylstyrene with acrylonitrile, the proportion of acrylonitrile being from 10 to less than 28% by weight,

   b: from 0 to 80% by weight, based on the entirety of components A + B, of at least one graft copolymer B made from

      b1: as component B1, from 10 to 90% by weight of at least one elastomeric particulate graft base with a glass transition temperature below 0°C, and

      b2: as component B2, from 10 to 90% by weight of at least one graft made from polystyrene or from a copolymer of styrene and/or α-methylstyrene with acrylonitrile, the proportion of acrylonitrile being from 10 to less than 28% by weight,

   where the entirety of the components A + B used is from 10 to 100 parts by weight, based on the total weight of the components used,

   c: as component C, from 0.05 to 5 parts by weight, based on the total weight of the components used, of a phyllosilicate,

   d: as component D, from 0 to 90 parts by weight, based on the total weight of the components used, of at least one polycarbonate, and

   e: as component E, from 0 to 20 parts by weight, based on the total weight of the components used, of other conventional auxiliaries and fillers, and

   wherein the phyllosilicate is mica.

10. The method as claimed in claim 9, wherein the chemical resistance is improved with respect to chemicals selected from alcohols,

C_3-C_8 alkanes, gasoline, premium gasoline, diesel, halogenated hydrocarbons, hypochlorite salts, and sodium dichloroisocyanate dihydrate.

14. The method as claimed in claim 9, wherein the proportion of acrylonitrile is from 18 to 27% by weight.

15. A thermoplastic molding composition built up from components A, C, and where appropriate, B, D and E, using

    a: as component A, from 20 to 100% by weight, based on the entirety of components A + B, of a hard component made from one or more copolymers of styrene and/or α-methylstyrene with acrylonitrile, the proportion of acrylonitrile being from 10 to less than 28% by weight,

    b: from 0 to 80% by weight, based on the entirety of components A + B, of at least one graft copolymer B made from

        b1: as component B1, from 10 to 90% by weight of at least one elastomeric particulate graft base with a glass transition temperature below 0°C, and

        b2: as component B2, from 10 to 90% by weight of at least one graft made from polystyrene or from a copolymer of styrene and/or α-methylstyrene with acrylonitrile, the proportion of acrylonitrile being from 10 to less than 28% by weight,

    where the entirety of the components A + B used is from 10 to 100 parts by weight, based on the total weight of the components used,

    c: as component C, from 0.05 to 5 parts by weight, based on the total weight of the components used, of a phyllosilicate,

    d: as component D, from 0 to 90 parts by weight, based on the total weight of the components used, of at least one polycarbonate, and

    e: as component E, from 0 to 20 parts by weight, based on the total weight of the components used, of other conventional auxiliaries and fillers,

    wherein the phyllosilicate is mica.

16. A thermoplastic molding composition as claimed in claim 15, wherein the proportion of acrylonitrile is from 18 to 27% by weight.

17. A process for preparing the styrene polymers with improved chemical resistance as claimed in claim 15, which comprises separately preparing components A and C, and, where appropriate, components B, D, and E, combining component A with component C, and intimately mixing and then extruding the same with components B, D, and E, as appropriate.

21. A method for improving the chemicals resistance, reducing the swelling, and improving the stress-cracking resistance of styrene copolymers, which comprises adding to said copolymers an effective amount of mica.

PTO's copies

re BARGHOORN et al
SN 09/936,353
PF 49819

Ullmann's Encyclopedia of Industrial Chemistry

Fifth, Completely Revised Edition

Volume A 7:
Chlorophenols to Copper Compounds

Executive Editor: Wolfgang Gerhartz
Senior Editor: Y. Stephen Yamamoto
Editors: F. Thomas Campbell, Rudolf Pfefferkorn,
James F. Rounsaville

pp 109–113
126–133

VCH

Numerical data, descriptions of methods or equipment, and other information presented in this book have been carefully checked for accuracy. Nevertheless, authors and publishers do not assume any liability for misprints, faulty statements, or other kinds of errors. Persons intending to handle chemicals or to work according to information derived from this book are advised to consult the original sources as well as relevant regulations in order to avoid possible hazards.

Production Director: Maximilian Montkowski
Production Manager: Myriam Nothacker

Library of Congress Card No. 84-25-829

Deutsche Bibliothek, Cataloguing-in-Publication Data:

Ullmann's encyclopedia of industrial chemistry / executive ed.: Wolfgang Gerhartz. Senior ed.: Y. Stephen Yamamoto. Ed.: F. Thomas Campbell ... [Ed. advisory board Hans-Jürgen Arpe ...]. — Weinheim ; New York, NY : VCH
Teilw. mit d. Erscheinungsorten Weinheim, Deerfield Beach, Fl.
Bis 4. Aufl. u. d. T.: Ullmanns Enzyklopädie der technischen Chemie

NE: Gerhartz, Wolfgang [Hrsg.]; Encyclopedia of industrial chemistry

Vol. A. Alphabetically arranged articles.
7. Chlorophenols to copper compounds. — 5th, completely rev. ed. — 1986.

ISBN 3-527-20107-6 (Weinheim);
ISBN 0-89573-157-6 (New York)

Distribution: VCH Verlagsgesellschaft, P.O. Box 1260/1280. D-6940 Weinheim (Federal Republic of Germany)
USA and Canada: VCH Publishers, 220 East 23rd Street, Suite 909, New York NY 10010 (USA)

Cover design: Wolfgang Schmidt
Composition, printing, and bookbinding: Graphischer Betrieb Konrad Triltsch, D-8700 Würzburg
Printed in the Federal Republic of Germany

Clays

HAYDN H. MURRAY, Indiana University, Department of Geology, Bloomington, Indiana 47405, United States

The term *clay* has a double meaning and, therefore, should be defined when it is used. Clay is used both as a rock term and as a particle size term. As a rock term, clay is used for a natural, earthy, fine-grained material composed largely of a limited group of crystalline minerals known as the clay minerals. As a particle size term, clay is used for the category that includes the smallest particles. Soil investigators and mineralogists generally use 2 µm as the maximum size, although the Wentworth scale [1] defines clay as material finer than 4 µm. GRIM [2] uses the term clay material for any fine-grained, natural, earthy, argillaceous material; in this way, the term can include clays, shales, or argillites, and some soils if they are argillaceous.

Clay is an abundant raw material and has an amazing variety of uses and properties that depend on the clay mineral composition and other factors enumerated by GRIM [2]. These factors are clay mineral composition, nonclay mineral composition, presence of organic material, the type and amount of exchangeable ions and soluble salts, and texture.

Clays are comprised of certain groups of hydrous aluminum, magnesium, and iron silicates that may contain sodium, calcium, potassium, and other ions. These silicates are called the clay minerals, and the major clay mineral groups are kaolins, smectites, illites, chlorites, and hormites. The specific clay minerals are identified by several techniques, including X-ray diffraction [3], differential thermal analysis [4], electron microscopy [5], and infrared spectrometry [6]. Identification and quantification of the clay minerals and nonclay minerals present in a clay material is important because the uses and engineering properties are controlled largely by these two factors.

Clays and clay minerals are important geologically, industrially, and agriculturally; they are important to the engineer in building foundations, tunnels, road cuts and fills, and dams. There are several scientific groups whose work is largely devoted to clays, including AIPEA (Association Internationale pour l'Étude des Argiles), Clay Minerals Group of the Mineralogical Society of Great Britain, CMS (Clay Minerals

Society, United States), European Clay Minerals Society, Clay Minerals Society of Japan, and the Australian Clay Minerals Society. Major publications include the *Proceedings of International Clay Conferences*, published by AIPEA; *Clays and Clay Minerals*, published by CMS; *Clay Minerals*, published by the Mineralogical Society of Great Britain; and *Clay Mineral Science*, published by the Japanese clay group.

1. Structure and Composition of Clay Minerals

GRIM [2] proposed a tentative classification based on the structural attributes of the various clay minerals. This classification is relatively simple:

I. Amorphous
   Allophane group [*12172-71-3*]
II. Crystalline
   A. Two-layer types (sheet structures composed of units of one layer of silica tetrahedrons and one layer of alumina octahedrons)
      1. Equidimensional
         Kaolin group [*1332-58-7*]
            kaolinite [*1318-74-7*], dickite [*1318-45-2*], nacrite [*12279-65-1*]
      2. Elongate
         halloysite [*12244-16-5*]
   B. Three-layer types (sheet structures composed of two layers of silica tetrahedrons and one central dioctahedral or trioctahedral layer)
      1. Expanding lattice
         Smectite group [*12199-37-0*]
            a. Equidimensional
               montmorillonite [*1318-93-0*], sauconite [*12424-32-7*], vermiculite [*1318-00-9*]
            b. Elongate
               nontronite [*12174-06-0*], saponite [*1319-41-1*], hectorite [*12173-47-6*]
      2. Nonexpanding lattice
         Illite group [*12173-60-3*]
   C. Regular mixed-layer types (ordered stacking of alternate layers of different types)
      Chlorite group
   D. Chain-structure types (hornblende-like chains of silica tetrahedrons linked together by octahedral groups of oxygens and hydroxyls containing aluminum and magnesium ions)
      Hormite group
         palygorskite [*12174-11-7*] (attapulgite [*1337-76-4*]), sepolite [*15501-74-3*]

The materials described as *allophane* are amorphous [7] and contain variable proportions of silica, alumina, and water. Allophane is commonly associated with halloysite and generally has a glassy appearance.

The kaolin minerals [8] are hydrous aluminum silicates and have the approximate composition $2\,H_2O \cdot Al_2O_3 \cdot 2\,SiO_2$. *Kaolinite* is the most common of the kaolin minerals. The structure of kaolinite consists of a single silica tetrahedral sheet and a single alumina octahedral sheet combined to form the kaolin unit layer (Fig. 1). These unit layers are stacked on top of each other. Variations in orientation of the unit layers in stacking cause differences in the kaolin mineral itself and lead to the differentiation of *nacrite* and *dickite* in the kaolin group [2]. Platy and vermicular forms of kaolinite are shown in the electron micrograph in Figure 2.

Halloysite is an elongate mineral that occurs in a hydrated and dehydrated form [7]. BATES et al. [9] proposed that the hydrated form of halloysite consists of curved sheets of kaolin unit layers

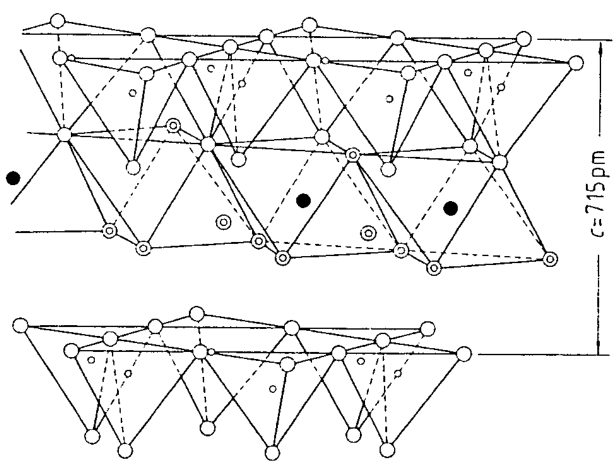

Figure 1. Structure of kaolinite
○ Oxygen; ◎ Hydroxyl; o Silicon tetrahedrally coordinated; ● Aluminum octahedrally coordinated

Figure 2. Scanning electron micrograph of kaolinite stacks and plates

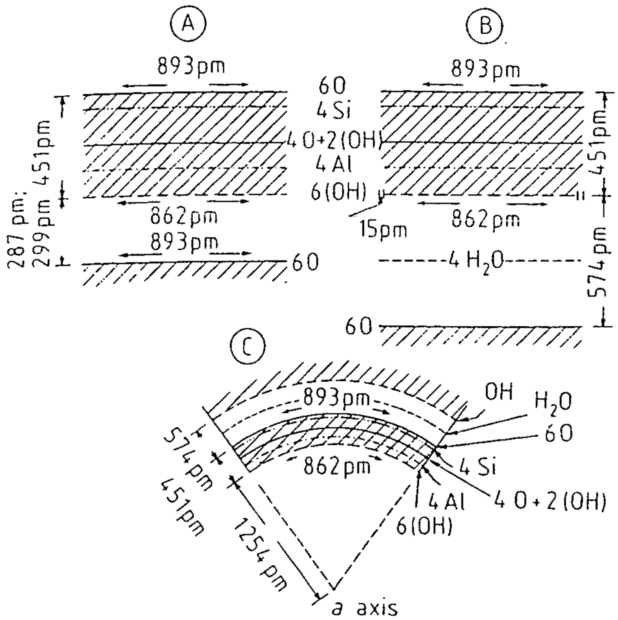

Figure 3. Structure of halloysite
A) Dehydrated halloysite; B) Hydrated halloysite; C) Proposed curved structure of halloysite

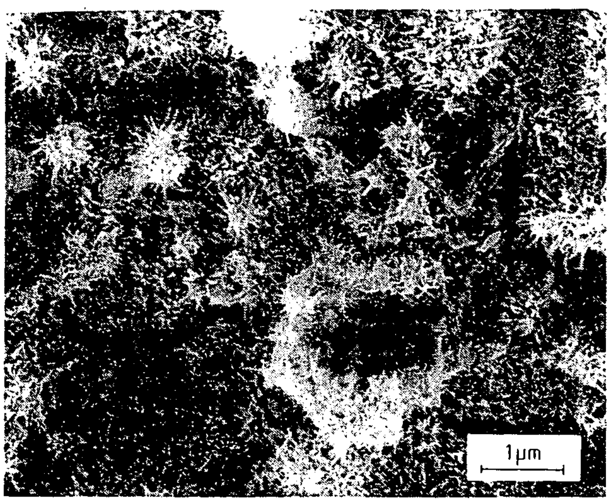

Figure 4. Scanning electron micrograph of elongate halloysite growing on feldspar

(Fig. 3), which is consistent with electron micrographs (Fig. 4).

Smectite is composed of units consisting of two silica tetrahedral sheets with a central alumina octahedral sheet. The lattice has an unbalanced charge because of substitution of alumina for silica in the tetrahedral sheet and iron and magnesium for alumina in the octahedral sheet. Because of this and because oxygen layers are adjacent when these unit layers are stacked, the attraction holding these layers together is weak, and cations and polar molecules can enter between the layers and cause expansion (Fig. 5). Sodium *montmorillonite* is a smectite in which sodium and water molecules are the interlayer material, and calcium montmorillonite is a smectite in which calcium and water molecules are the interlayer material. Figure 6 shows an electron micrograph of a sodium montmorillonite.

Sauconite is a smectite in which zinc has replaced some of the aluminum. *Nontronite* results when iron replaces the aluminum, and *saponite* results when magnesium replaces aluminum. *Hectorite* results when magnesium replaces aluminum and lithium is the ion between the layers.

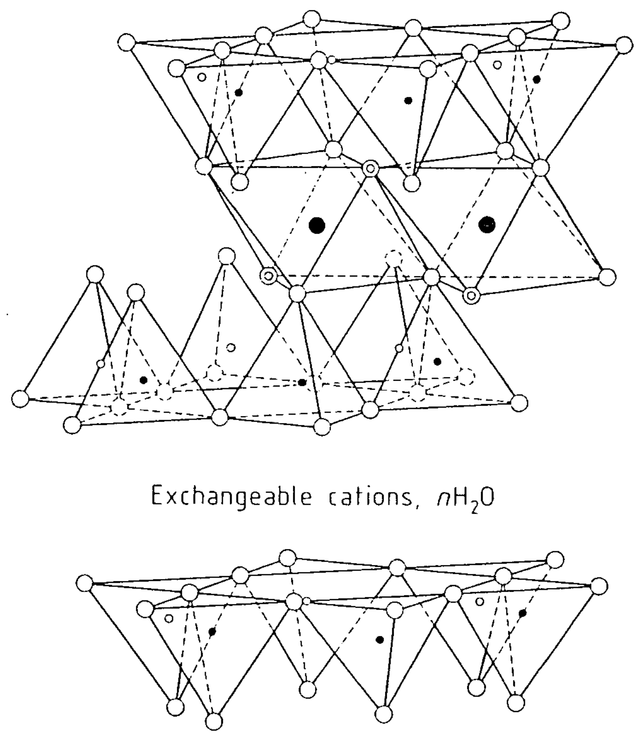

Figure 5. Structure of smectite
○ Oxygen; ◎ Hydroxyl; ● Aluminum, iron, magnesium; ○● Silicon, occasionally aluminum

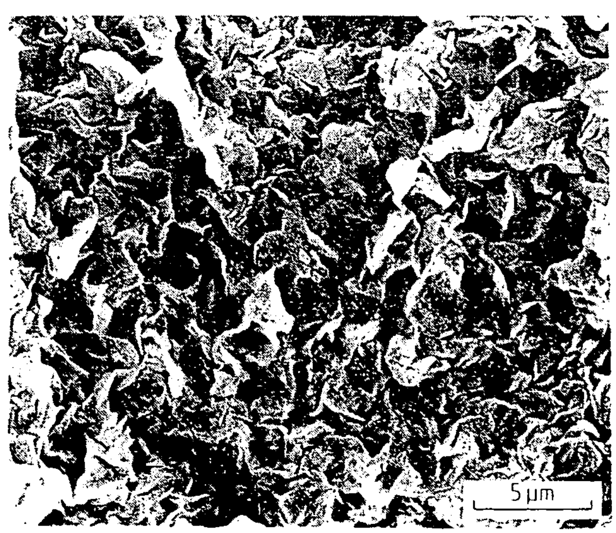

Figure 6. Scanning electron micrograph of a sodium montmorillonite (Wyoming)

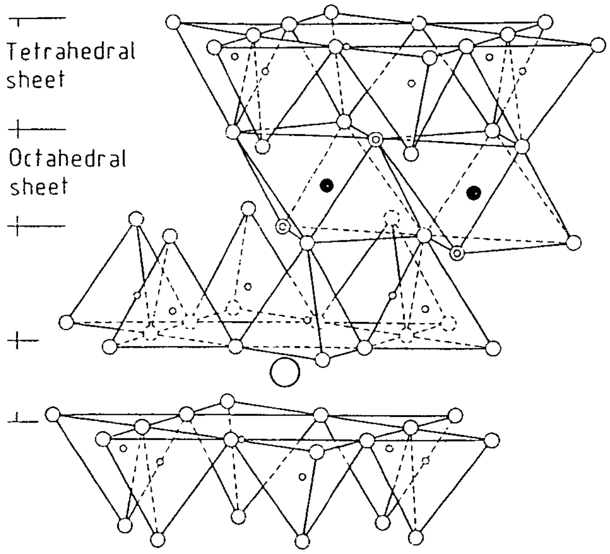

Figure 7. Structure of illite
○ Potassium; ○ Oxygen; ● Aluminum (only 2/3 of available positions filled); ◎ Hydroxyl; o Silicon (1/4 replaced by aluminum)

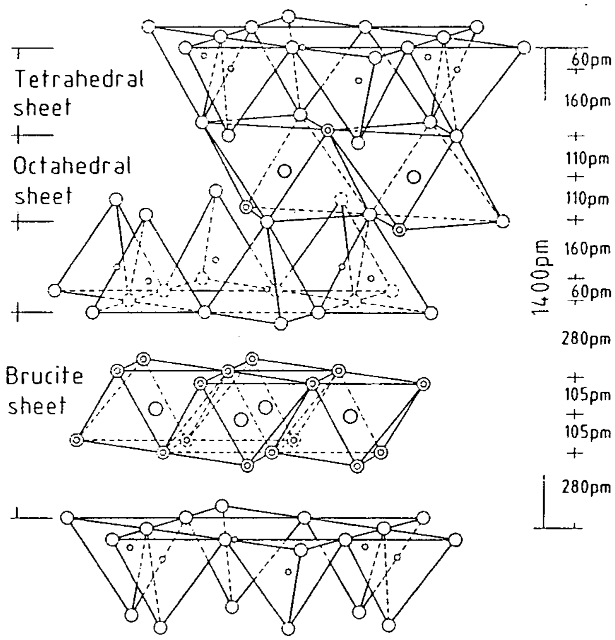

Figure 8. Structure of chlorite
○ Magnesium, iron (all available positions filled); ◎ Hydroxyl; ○ Oxygen; ∘ Silicon (1/4 replaced by aluminum)

Vermiculite is an equidimensional expandable clay mineral. The structure [10] consists of a layer made up of two silica tetrahedral sheets with a central magnesium–iron octahedral sheet separated by two layers of water molecules and adsorbed magnesium and calcium ions. Vermiculite differs from montmorillonite in that the layers do not expand as much and show less random stacking [2].

Illite is a general term for the micalike clay mineral [11]. The basic structural unit is a layer composed of two silica tetrahedral sheets and a central octahedral sheet. The unit is similar to that of montmorillonite except that more aluminum ions replace silicon in the tetrahedral sheet, which causes a charge deficiency. This charge deficiency is balanced by potassium ions that act as a bridge between the unit layers and bind them together so that illites are nonexpandable (Fig. 7).

Another common group of clay minerals is the *chlorite* minerals. The structure consists of alternate mica layers and brucite layers (Fig. 8). The brucite-like layer can be a magnesium, aluminum, or iron hydroxide, or a combination of all three. The various members of the chlorite group are differentiated on the kind and amount of substitution in the brucite and the mica layers [12].

The hormite clay minerals *palygorskite* (attapulgite) and *sepiolite* have a chainlike structure (Fig. 9). Palygorskite and attapulgite [13] are synonymous, palygorskite being the preferred name. The differentiation between sepiolite and palygorskite is the substitution of iron for magnesium, which causes some minor structural differences. These minerals consist of double silica tetrahedral chains linked together by octahedral oxygen and hydroxyl groups containing aluminum and magnesium ions. An electron micrograph of palygorskite is shown in Figure 10.

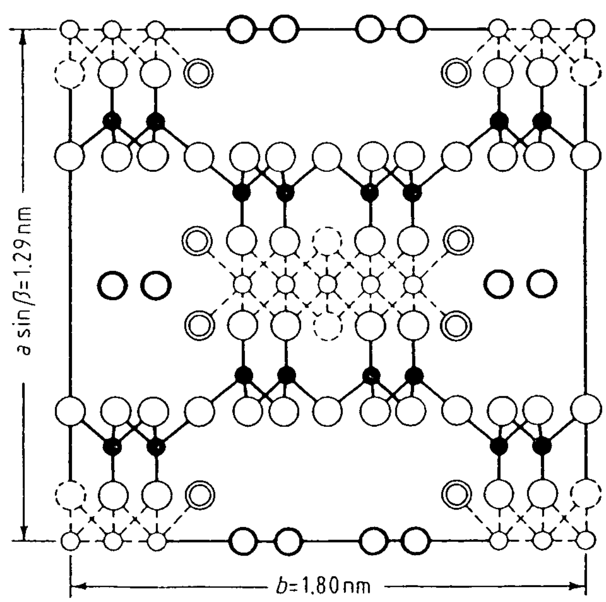

Figure 9. Structure of palygorskite (attapulgite), $(OH_2)_4(OH)_2Mg_5Si_8O_{20} \cdot 4\,H_2O$
○ H_2O; ⬚ Hydroxyl; ○ Magnesium or aluminum; ◎ OH_2; ○ Oxygen; ● Silicon

Figure 10. Scanning electron micrograph of palygorskite (attapulgite)

Mixed-layer clays are mixtures of the unit layers on a layer-by-layer basis and are relatively common in nature. Illite–smectite, illite–chlorite, smectite–chlorite, vermiculite–illite, and even smectite–kaolinite have been described. Mixed-layer clays with both random and regular layering were treated by REYNOLDS [14].

2. Geology and Occurrence of Major Clay Deposits

Certain clays, such as kaolins, smectites, and hormites, can be found in relatively pure occurrences or can be beneficiated to relatively high purity. These particular clays have special industrial applications. Illites and chlorites are usually in shales or clays that are used for structural clay ceramics; they are not utilized where the application depends on the particular physical or chemical properties of the individual clay mineral.

2.1. Kaolin

Kaolin is a rock term, a clay mineral group, and an industrial mineral commodity. It is used interchangeably with the term china clay. The term kaolin is derived from the Chinese word *kauling*, meaning high ridge, the name for a hill near Jauchau Fu in China where a kaolin clay was mined for many centuries. Kaolin is a clay that

1) consists of substantially pure kaolinite or related clay minerals;
2) is naturally or can be beneficiated to be white or nearly white;
3) fires white or nearly white; and
4) is amenable to beneficiation by known methods to make it suitable for use in whiteware, paper, rubber, paint, and similar uses.

The term is applied without direct relation to the purity of deposits. Many large kaolin deposits are essentially pure and require little concentration during preparation for market. Most, however, are slightly off-color and require beneficiation to improve the brightness and whiteness and to control the particle size. Other kaolins contain as little as 10% kaolinite; these must be washed and concentrated to recover a marketable product.

Kaolin deposits are classed as primary or secondary. Primary or residual kaolins are those that have formed by the alteration of crystalline rocks such as granite and remain in the place where they formed. Secondary deposits of kaolin are sedimentary and have been transported from their place of origin and deposited in beds or lenses associated with other sedimentary rocks

Table 1. Geologic eras, periods, and epochs

Eras	Periods	Epochs	Years ago
Cenozoic	Quaternary	Holocene	
		Pleistocene	
	Tertiary	*Pliocene*	
		Miocene	
		Oligocene	
		Eocene	
		Paleocene	70×10^6
Mesozoic	*Cretaceous*	*Upper*	
		Lower	
	Jurassic		160×10^6
	Triassic		
Paleozoic	Permian		230×10^6
	Pennsylvanian		
	Mississippian		
	Devonian		
	Silurian		
	Ordovician		
	Cambrian		

The terms in italics are mentioned in the text.

When palygorskite (attapulgite) is to be used for salt-water drilling mud, the clay is extruded at high pressure through small orifices. This shears apart the bundles of palygorskite into individual elongate particles, which produces a higher viscosity drilling fluid.

4. Properties and Uses

Kaolins, smectites, hormites, and miscellaneous clays form an important industrial minerals group. Because of their fine particle size, particle shape, and surface chemistry, they have unique colloidal and physical properties.

4.1. Kaolin

Kaolin is one of the most versatile of the industrial minerals [82] and is used extensively for many applications [83]. It is a unique industrial mineral because it

1) is chemically inert over a relatively wide pH range (except for catalytic activity in some organic systems);
2) is white or near white;
3) has good covering or hiding power when used as a pigment or extender in coating and filling;
4) is soft and nonabrasive;
5) has low conductivity of both heat and electricity; and
6) is lower in cost than most materials with which it competes.

Some uses of kaolin require rigid specifications, including particle size, brightness, color, and viscosity. On the other hand, some uses have no critical specifications, e.g., cement, where the only concern is light color and chemical composition. Ceramic specifications are variable in that individual users may have different requirements as to strength, plasticity, fired color, shrinkage, and pyrometric cone equivalent (PCE). The major process industries in which kaolin finds a substantial use are paper, paint, ceramics, rubber, plastics, ink, catalyst, and fiberglass, as well as some special uses.

4.1.1. Physical Properties

Diagnostic tests are used to evaluate kaolin physical properties [84]. Some properties that can be used as screening tests for the many potential uses for kaolin are as follows:

mineralogy
screen residue (grit)
particle-size distribution
brightness
viscosity
pH

Mineralogy. The mineral content of a kaolin is important in assessing the uses, the results of many tests determining the physical properties, and the beneficiation processes that may be needed to produce a saleable product. X-ray diffraction of the whole sample gives a quick assessment of the gross mineralogy, but in many instances minor quantities of illite and smectite are not detected. Separation of the 2-μm and 0.5-μm fractions and preparation of oriented slides for X-ray enhances the basal reflections of the clay minerals and enables the detection of very small quantities of smectite and illite.

The presence of quartz, cristobalite, alunite, smectite, illite, muscovite, biotite, chlorite, gibbsite, feldspar, anatase, pyrite, iron oxides and hydroxides, and halloysite affects the beneficiation processes and the possible uses of the kaolin. In many instances, the presence of halloysite in a kaolin cannot be detected by X-ray diffraction; therefore, electron micrographs and differential thermal analysis must be used.

Screen Residue. The grit test gives the percentage of particles that are retained on a 325-mesh screen (44-μm openings). Quartz and mica, along with hard agglomerates of kaolin, are the most common minerals retained on the screen. The amount of screen residue is important in estimating the recovery of the minus 325 mesh material since this is the fraction that is the usable portion of the kaolin. Generally, if the kaolin contains more than 5–8 % grit, it cannot be dry processed.

Particle-Size Distribution. Particle-size distribution (Fig. 26) is one of the more important properties of a kaolin because it affects viscosity, brightness, opacity, gloss, ceramic strength and shrinkage, and many other properties. Sedimentation methods based on Stoke's law of settling are used for measuring particle size. The 2-μm content of a kaolin is particularly important because it is this fraction that constitutes the major

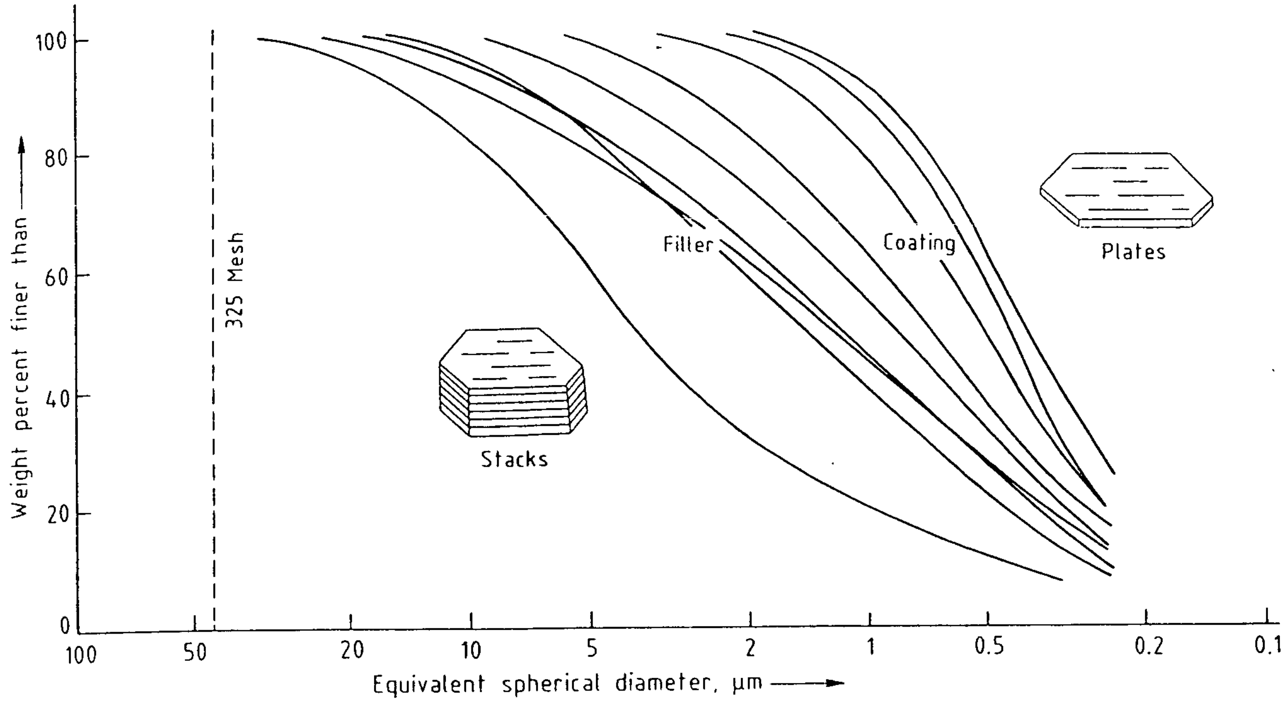

Figure 26. Particle-size distribution of some typical kaolin coating and filler grades

portion of paper coating clays and high-glossing paint clays. The particle-size distribution also determines the beneficiation procedures that are used in processing a kaolin for industrial uses.

Brightness. The brightness of a kaolin is an important property because it determines the potential uses and prices. In general, the higher the brightness of the kaolin the more value the kaolin has. Standard brightness values are measured at a wavelength of 457 nm, and a common standard against which the samples are compared is smoked magnesium oxide. As a general rule, filler clays have a brightness of 80–85%, and paper coating clays and high-glossing paint clays have a brightness of 85–90%.

Viscosity. The flow properties of kaolin used for paper coating are very important. Both low-shear and high-shear viscosity measurements are made at 70–71% solids. Low-viscosity kaolins are required for paper coating because the kaolin coating color must flow easily as it is applied to the paper surface, not leaving streaks or blotches, which can be caused by high-viscosity coating colors.

pH. The pH of untreated kaolin slurries normally ranges from 4.5 to 6.5. A high pH generally indicates the presence of soluble salts that can cause problems in many applications.

4.1.2. Paper

The mineral kaolinite has many physical properties that are advantageous to the paper industry. It is white, fine, soft and nonabrasive, and relatively inert. In the United States, ca. 70% of all of the wet processed kaolin is used by the paper industry as a coating clay and as a filler. Some physical constants that are representative of kaolins from Georgia are the following:

Specific gravity d_4^{20}	2.62
Index of refraction	1.57
Hardness (Mohs' scale)	1.5–2
Fusion temperature, °C	1850
Valley abrasion number	4–10
Dry brightness (at 457 nm), %	75–91
Crystal system	triclinic

The Georgia kaolins and English kaolins are the most widely used kaolins in the paper industry. Table 2 gives typical chemical analyses of two Georgia kaolins and an English kaolin.

Important Properties. *Particle-size* and *shape distribution* are probably the most important factors in controlling the many physical properties of kaolin important to the papermaker. Figure 26 shows the range of particle-size distributions available commercially. The 2-µm size is used as the commercial control point. The coarse particle size kaolins are normally used as filler

Table 2. Typical chemical analyses, wt%

Component	Cretaceous middle Georgia kaolin	Tertiary east Georgia kaolin	English kaolin	Theoretical kaolin
SiO_2	45.30	44.00	46.77	46.3
Al_2O_3	38.38	39.5	37.79	39.8
Fe_2O_3	0.30	1.13	0.56	
TiO_2	1.44	2.43	0.02	
MgO	0.25	0.03	0.24	
CaO	0.05	0.03	0.13	
Na_2O	0.27	0.08	0.05	
K_2O	0.04	0.06	1.49	
Ignition loss	13.97	13.9	12.79	13.9

clays, and the fine particle size kaolins are used as coating clays.

Some of the properties of importance to the papermaker are dispersion, rheology, brightness and whiteness, opacity, gloss and smoothness, orientation, adhesive demand, film strength, and ink receptivity.

Complete *dispersion* of the kaolin particles is necessary to obtain maximum efficiency in a coating or filler clay. Kaolin is easily dispersed because of its hydrophilic surface. In the natural state, kaolin is acid and is flocculated. This flocced state is the result of the presence of both positive and negative charges on the particles, which attract each other and form aggregates. Therefore, dispersing agents must be used to deflocculate the kaolin by making the particles all the same charge order, thus obtaining maximum fluidity. The most efficient dispersing agents for kaolin in aqueous systems are alkali-metal polyphosphates, polyacrylates, and silicates [85].

The *rheology* or flow properties of coating clays and coating colors are complex and exert a controlling influence on the coating operation. Such factors as coat weight, smoothness, and freedom from pattern on the coated sheet are related to viscosity. Low-viscosity kaolins can be dispersed (made down) readily at high solids concentration (71 %). In addition, these low-viscosity suspensions can be pumped and screened with relative ease. The coating process (i.e., trailing blade, roll coater, air knife, etc.), the coating color formula, the type and amount of adhesive, and the percent solids of the coating color determine the high- and low-shear viscosity values that can be tolerated for the coating clay.

Brightness and *whiteness* of kaolin coatings are controlled primarily by the presence of iron and titanium minerals in the kaolin. However, the coating structure is also important. Significant differences in refractive indices between coating components are necessary to obtain maximum light scattering and, thus, optimum brightness and whiteness. The coating structure must have a maximum of uniformly distributed air-filled pores. Differences in brightness of one percentage point of the dry kaolin powder may result in a difference of less than 0.2 % brightness of the coated sheet. Coating structure and weight, particle-size distribution, particle shape, and brightness and whiteness of the dry kaolin powder all affect the coated sheet brightness and whiteness.

Opacity of kaolin coatings is strongly influenced by particle packing, which depends largely on particle size and shape and particle-size distribution. Particle size and particle-size distribution must be optimal to develop efficient scattering of light and consequent opacity. The presence of ultrafine particles of ca. 0.1 µm seriously lowers the opacity [86]. The opacity of the coating layer depends on the difference in the refractive indices and the relative proportions of the various components, including air, pigment, and adhesive.

Gloss and *smoothness* are related to particle size and shape. Superior gloss is attained with kaolins of fine particle size. Smoothness is developed with fine, thin, small-diameter particles. The object of coating paper is to smooth over the fine structure of the base paper to make high-quality ink transfer possible.

Parallel *orientation* of the kaolin particles results in conformation to substrate irregularities, thus reflecting imperfections of the substrate surface. The method of application of the coating affects the orientation and, hence, the smoothness. For optimum effects on irregular substrates, the particle orientation should be random adjacent to the substrate and parallel at the top of the coating [87].

Coating clays are characterized by a low *adhesive demand*, ranging between 10 and 18 %. Finer particle size clays require slightly higher amounts of adhesive. The introduction of adhesive can disrupt orientation and reduce smoothness, gloss, and other optical qualities. The selective drainage of adhesive into the substrate or the concentration at the coating surface strongly affects the coating properties [87]. The adhesive

requirement is directly related to the surface area of the clay. The amount of adhesive in the coating affects the opacity, brightness, color, and smoothness, as well as film strength. If the amount of adhesive is excessive, the printability is poor.

Film strength is related to preferential adhesive migration into the substrate and to the preferred orientation of the kaolin particles [88]. Maximum film strength is attained with well-oriented, dense films, which imply a highly bonded surface area. If pick occurs within the coating layer, it is generally caused by insufficient adhesive, excessive adhesive migration into the base sheet, or poorly dispersed pigment.

Kaolins are considered to have low ink absorption even though they readily accept printing inks. Substantial differences exist between the *ink receptivity* of coatings made from different grades of kaolin. This is related to film permeability, which is influenced by void volume. Thus, small-diameter particles that are randomly oriented give excellent ink receptivity. The interrelationship of the kaolin and adhesive is a major control over ink receptivity and holdout.

There are many grades of coating and filler clays available to the paper industry. The properties that define these coating and filler clays are based on brightness, particle size and particle-size distribution, and particle shape. Table 3 shows the major coating grades and their particle size and brightness.

Table 3. Particle size and brightness of Georgia coating kaolins

Grades	Mass fraction with particle size < 2 μm, %	Brightness, %
Regular coating clays		
No. 3	73	85.0–86.5
No. 2	80–82	85.5–87.0
No. 1	90–92	87.0–88.0
Fine no. 1	95	86.0–87.5
Delaminated coating clays		
Regular	≈70–80	88.0–90.0
Fine	≈90–95	87.0–88.0
High-brightness coating clays		
No. 2	80	89.0–91.0
No. 1	92	89.0–91.0
Fine no. 1	95	89.0–91.0
Special coating clays		
Low-glossing clays	≈50	87.0–88.0
Calcined extender	85	92.5–94.0

Coating Clays. The no. 3 and no. 2 grades are generally used in high-solids formulations for publication-grade paper and medium-finish lower cost enamels. Slick sheet magazines with large circulation are generally coated with one of these two regular grades often mixed with the regular delaminated grade. The no. 1 grade is used to coat high-quality boxboard and enamel papers. This grade gives excellent gloss and brightness and relatively uniform ink receptivity and good smoothness. The fine no. 1 grade is used where maximum gloss and very good ink holdout is desired.

The regular delaminated grade is used on lightweight paper and paper that has a rough surface where good printability must be maintained. This clay gives coatings that are exceptionally smooth with excellent ink and varnish holdout. The fine delaminated grade is used to achieve maximum gloss, good runnability, and high opacity.

The high-brightness grades, having a blue-white tint, are very bright. The coatings that use these grades are very smooth and give excellent gloss ink holdout and good printability. These high-brightness grades are used to coat premium-grade paper.

The special coating grades were developed to meet specific coating needs. The low-glossing coating clays are used when a dull or matte finish is required. The calcined kaolin extender is used to replace titanium dioxide in the coating to reduce the cost of the coating formulation and still maintain the desired optical properties.

Filler Clays. Fillers are highly desirable in printing papers because they increase the opacity, raise the brightness, increase the smoothness or finish, and improve the ink receptivity and printability. Filler clays also improve the appearance and absorbency of paper, as well as increase the density. A perfect filler, if available, would have the following characteristics [89]:

1) Reflectance of 100% at all wavelengths of light
2) High index of refraction
3) Grit-free and a particle size close to 0.3 μm, approximately half the wavelength of light
4) Low specific gravity, soft, and nonabrasive
5) Ability to impart to paper a surface capable of taking any finish, from the lowest matte to the highest gloss
6) Complete retention in the paper web
7) Completely inert and insoluble
8) Reasonable in price

Obviously, such a perfect filler is not available, and filling paper is a matter of compromise.

Table 4. Filler grades of kaolin

Type	Brightness, %	Screen residue, %
Air-floated filler	80–81	0.30
Whole clay filler	81–83	0.10
Whole clay filler	83–85	0.10
Water-washed filler	81–83	0.09
Water-washed filler	83–84	0.09
Water-washed filler	84–86	0.05
Delaminated filler	86–87	0.005
High-brightness delaminated filler	87–89	0.005
Calcined kaolin extender	91–94	0.01

Kaolin is the usual filler in white or essentially white papers such as newsprint, printing grades, uncoated book, to develop certain desirable properties, and in paper may be the only filler used. In some grades, kaolin may be partially replaced by other mineral fillers to develop certain desirable properties, or may be used alone without clay.

In general, the lighter the weight of the paper, the greater the need for a filler to improve its opacity and brightness. Cost reduction is an important criterion for using fillers. In most cases, the filler is much less expensive than the pulp it replaces. Table 4 gives the filler grades of kaolin that are available.

In general, filler grades are produced to meet brightness and grit specifications. The lowest price filler grade is air-floated, whereas the highest price filler grade is the calcined kaolin extender. A good review of the properties of paper affected by fillers is presented by Casey [90] (→ Paper).

4.1.3. Paint

Kaolins are used extensively in water-based paints. Kaolin is a functional extender pigment that has good covering or hiding power, imparts desirable flow properties to the paint, and is inexpensive. *Brightness* and *particle size* are important physical properties, as is a *resistivity specification*. A resistivity test gives an index of the amount of residual soluble salts that remain in the clay. Higher resistivity values reflect a low soluble salt content, which is important because high soluble salt content adversely affects the dispersion of the paint ingredients and alters paint properties.

Another important physical property is *oil absorption*, which gives an indication of surface area and which is related to a parameter called vehicle demand. A test commonly used by the paint manufacturer to measure dispersion is a fineness of grind measurement using a Hegman gage. Actual paint formulations are made, and many performance tests are run, including gloss, color, smoothness, flow characteristics, dispersion, stability, weathering characteristics, aging, washability, and hiding power.

The kaolins used in paint vary from very coarse, which produces a matte finish, to very fine, which gives a high-gloss finish. Calcined kaolins are used in paint as a titanium dioxide replacement and extender. Delaminated clays are used to give a high-gloss finish with good covering power, good color, and excellent washability (→ Paints and Coatings).

4.1.4. Ceramics

The ceramic industry is a large user of kaolin clays in whiteware, sanitary ware, insulators, and refractories. Several tests are used to evaluate kaolins for use in ceramics, including plasticity, shrinkage, modulus of rupture, absorption, fired color, casting rate, PCE (see p. 126), and chemical analysis.

Coarse-particle-size clays are used for casting clays in sanitary ware, and fine-particle kaolins are used when high strength is important, such as in whiteware and as a bond in certain refractory applications. Ball clays, which are a fine-particle-size, very plastic kaolinitic clay, are used in whiteware, stoneware, enamels, etc. Calcined kaolin called grog is marketed to the refractory industry for use in high-alumina refractories. Both dry-process and wet-process kaolins are used by the ceramic industry (→ Ceramics, General Survey).

4.1.5. Rubber

Kaolin is used by rubber manufacturers because of its reinforcing and stiffening properties and because of its low cost. Fine-particle-size kaolins give good resistance to abrasion and are used extensively in nonblack rubber goods. The kaolins that are used in rubber contain a maximum of 1 % free moisture. Both dry-process and wet-process kaolins are used, but by far the largest tonnage are dry-process grades. Brightness, particle size, and grit percentage are important physical properties. Other tests that are important in evaluating kaolin for use in rubber are water settling characteristics and oil absorption.

The water settling test gives a good idea of the reinforcing characteristics of the clay, and oil absorption also correlates with reinforcement. Tests on the clay-filled rubber itself are stress–strain, tear resistance, abrasion resistance, heat generation, energy rebound, extrusion and plasticity, hardness, aging characteristics, and water absorption [91] (→ Rubber).

4.1.6. Plastics

Kaolin is used in plastics because it aids in producing a smooth surface finish, reduces cracking and shrinkage during curing, obscures the fiber pattern when fiberglass is used as reinforcement, contributes to a high dielectric strength, improves resistance to chemical action and weathering, and helps control the flow properties. Kaolin is a functional filler in that it contributes some beneficial effects. Loadings in various plastic compositions vary from ca. 15% to as high as 60% (→ Plastics, General Survey).

4.1.7. Ink

Kaolin clays are used extensively in printing inks. In black inks the pigment is normally carbon black, but in white and other colored inks kaolin is a common extender pigment. The kaolins used in ink must be fine particle size and relatively white. A major disadvantage to the use of kaolin in ink is its hydrophilic nature. However, coating the kaolin particles with hydrophobic material increases its usefulness in inks. Surface-modified kaolins have found a significant market in printing inks (→ Drawing and Writing Materials).

4.1.8. Catalysts

Kaolin clays are used extensively in the production of cracking catalysts and molecular sieves. The kaolin clay should have relatively low iron and sulfate content. Although the surface of the kaolin does contribute some catalytic activity, the kaolin serves largely as a diluent for the silica–alumina gels [92]. Partially calcined kaolins, which are heated to a temperature just above the dehydroxylation temperature of ca. 600 °C, are used in the manufacture of molecular sieves [93] (→ Catalysis and Catalysts, Vol. A 5, pp. 313–367).

4.1.9. Fiberglass

Kaolin clays with a low iron content are used as a source of alumina and silica in the manufacture of fiberglass. A good grade of air-float kaolin is generally used (→ Fibers, Synthetic Inorganic).

4.2. Smectite

Smectite is a group name, and many minerals comprise the smectite group, including sodium montmorillonite, calcium montmorillonite, saponite, nontronite, hectorite, and sauconite. Each of these minerals has unique properties, and therefore, the individual smectite minerals and the other minerals that are present in the bentonite must be determined. This is done by X-ray diffraction, electron microscopy, differential thermal analysis, infrared spectrometry, and selective chemical analysis. Once the smectite mineral has been identified, then some of the properties can be established, for example, viscosity, thixotropy, plasticity, shrinkage, bonding strength, shear strength, and water impedance. These properties are not the same for all smectites and, in fact, are quite different.

The exchangeable cations present between the silica and alumina sheets (see Fig. 5, on p. 111) have a strong influence on the use and properties of the smectite. The major uses of smectites (bentonites) are in drilling muds, foundry sand bond, and iron-ore pelletizing. In addition to these three major uses, bentonite is used for many miscellaneous products, including filtering agents, water impedance, cosmetics, animal feed, pharmaceuticals, paint, ceramics, slurry trenching, catalysts, and decolorizing.

Drilling Fluids. Sodium montmorillonite, which is the major constituent of the Wyoming or Western bentonites, is a high-swelling clay with some unique properties. It is used throughout the world as an ingredient in drilling fluids because commonly this Western bentonite yields 100 barrels per ton (20 m^3/t) [31]. Only 5% of this bentonite is necessary to produce the high viscosity, thixotropy, and low filter-cake permeability required in the drilling fluid. Hectorite, the lithium smectite, also gives high yields and has excellent properties as an ingredient in drilling fluids. Some calcium montmorillonites can be treated with a sodium salt, usually soda ash,

to produce a bentonite suitable for use in drilling fluids, but in general such treatment does not substantially improve the water loss property of the bentonite.

Foundry Molding Sands. The molding sands used in foundries are composed of sand and clay. The clay provides bonding strength and plasticity. A small amount of tempering water is added to the mixture to make it plastic. It can then be molded around a pattern and be cohesive enough to maintain the shape after the pattern is removed and while molten metal is poured into it. The important foundry properties are green compression strength, dry compression strength, hot strength, flowability, permeability, and durability. These properties vary greatly with the amount of tempering water [31]. Both sodium and calcium bentonites (montmorillonites) are used as bonding clays. Calcium bentonite has a higher green strength, lower dry strength, lower hot strength, and better flowability than sodium bentonite. Final evaluations of the bonding clay can only be made after the bentonite is actually used in foundry practice so that flowability, durability, ease of shakeout of the casting from the mold, and cleanness of the surface of the cast metal can be determined. Commonly, blends of sodium and calcium bentonites are used to gain the optimum properties from each.

Iron-Ore Pelletizing. Bentonites are used extensively in pelletizing iron ores [94]. Finely pulverized ore concentrate must be pelletized into units of ca. 1 in. (2.5 cm) or more in diameter before it is used as blast furnace feed. Pelletized ore is a superior blast furnace feed. Bentonite is ca. 0.5 wt% of the ore. Because of its superior dry strength sodium bentonite is the preferred bentonite for pelletizing ores.

Other Uses. Acid-activated bentonites are widely used to *decolorize* mineral, vegetable, and animal oils. The clay also serves to deodorize, dehydrate, and neutralize the oils. In addition, the clay must have low oil retention and good filtration characteristics. It must not change the character of the oil nor give an objectionable taste to the oil. Some bentonitic clays naturally possess adequate decolorizing ability. Such materials are called fuller's earth. The bentonites that work best as both natural and acid-activation decolorizers are the calcium variety.

Some clay *catalysts* for cracking petroleum are produced from bentonites with very low iron content. The bentonite is reacted with sulfuric or hydrochloric acid at elevated temperatures followed by washing, drying, and calcining at ca. 500 °C. This process removes the adsorbed alkali metals and alkaline-earth metals along with the removal of iron and partial removal of magnesium and aluminum from the lattice. This increases the surface area and alters the pore-size distribution of the product. Calcium bentonite is the preferred material for making a smectite clay catalyst.

Sodium bentonites are used in *water impedance*. The clay is used to impede the movement of water through earthen structures such as dams, to stop seepage of water from ponds and irrigation ditches, and to stop water from entering basements of homes. One use of high-swelling sodium bentonite is in the slurry-trench or diaphragm-wall method of excavation in construction in areas of unconsolidated rock or soil [95]. In this method, the trench being excavated is filled with bentonite slurry, and the earth being excavated is removed through it. A thin filter cake on the walls of the excavation prevents loss of fluid, and the hydrostatic head of the slurry prevents caving and running of loose soil, which makes costly shoring unnecessary. Small amounts of sodium bentonites are added to cement to improve workability, lessen aggregate segregation, and enhance impermeability.

Sodium bentonites are widely used as *emulsifying* and *suspending agents* in many oil and water systems and in medicinal, pharmaceutical, and cosmetic formulations [96]. Sodium bentonites are used in both oil- and water-based paints. In water-based paints, the bentonite acts as a suspending and thickening agent. In oil-based paints, it is used as an emulsifying agent.

In *paper*, sodium bentonite is sometimes used in the deinking process to recover the cellulose fibers. These deinking processes generally involve heating the paper to be deinked in a caustic soda solution to break down the ink, thus freeing the ink pigment. Next a detergent is added to force the pigment from the paper fiber. Smectite is then added to disperse the pigment particles and adsorb them. Washing removes the smectite, which carries the ink pigment with it. Sodium bentonite is also used in papermaking to prevent the agglomeration of pitch, tar, wax, and resinous material. The addition of 0.5% smectite, based on the dry weight of the paper stock, pre-

vents agglomerates so that the globules will not stick to screens, machine wires, and press rolls and thus cause defects in the paper.

Sodium montmorillonite is the base for the organoclays described earlier. The organoclad clays are used in lubricating greases, inks, paints, and oil-based drilling fluids. These clays improve pigment suspension, viscosity, and thixotropy control. They also improve brushability and spraying characteristics of paints.

Calcium montmorillonite is used in adhesives; as granular pet litter; to clarify wines, cider, and beer; as floor absorbents; carriers and diluents in pesticide preparations; and in water clarification. White calcium smectites are used in detergents, paints, enamel suspensions, pharmaceuticals, cosmetics, food, pelletized animal feed, and in no-carbon-required copy paper [25].

Both calcium and sodium smectites are used as additives in ceramics, particularly because of their plasticity and relatively high green and dry strengths. For example, many brick clays are silty materials. The addition of a small amount of smectite improves the plasticity and green and dry strengths. In addition, both types are used as a liner for toxic and low-level radioactive waste disposal sites and as additives to latex for thickening and stabilizing.

4.3. Hormite

The use of the hormite clays is almost as varied as that of the kaolins and smectites. Because of the particle shape of the hormite clays, i.e., palygorskite (attapulgite) and sepiolite are elongate (see Fig. 10, on p. 113), they have some special applications. The specific type of hormite mineral can be identified with X-ray diffraction and is generally characterized by using scanning electron microscopy to determine the crystal size and length. In addition to the crystal shape, another set of important properties is the absorption and adsorption characteristics.

One of the more important, larger uses is *drilling fluids*. Considerable quantities of palygorskite and sepiolite are used in drilling fluids because the viscosity and gel strength of the mud are not affected by variations in electrolytic content as are those of muds comprised of bentonite. Thus, palygorskite and sepiolite drilling muds can be used with salt water or when formation brines become a serious problem. In recent years, the offshore drilling industry has used salt-water-based muds, so that the quantities of palygorskite and sepiolite used have increased dramatically.

Because palygorskite and sepiolite are not easily flocculated on account of their particle shape, these clay minerals are used as *suspending agents* in paint, medicines, pharmaceuticals, and cosmetics. In paint, palygorskite is used because it improves the thickening and thixotropic properties. Another major use is as *floor sweep compounds*, for absorbing oil and grease spills on factory floors, in service stations, and other areas where oil and grease spills are a problem. Granular particles of palygorskite are the most effective floor absorbent.

Palygorskite and sepiolite are also used extensively in *agriculture* as absorbents and adsorbents for chemicals and pesticides. The chemical is mixed onto the granular hormite clay particle, and the treated particle is placed in the ground with the seed particle. The pesticide or fertilizer chemical is slowly released to provide the necessary fertilizer or protection for the growing plant. Finely pulverized hormite clays are also used to adsorb chemicals, which can then be dusted or sprayed on the plant or on the surface of the ground.

Another large use for hormite clays is *pet litter*. Granular particles of hormite are an effective litter for absorbing animal waste, particularly for domestic cats. The clay effectively absorbs the waste and odors.

Haden [97] described the properties and uses of palygorskite and pointed out both the colloidal and noncolloidal characteristics that make this mineral important. Other uses of hormites include foundry sand binder, polishes, wax emulsions, metal drawing lubricants, laundry washing powders, bonding agents for granulation of powders, decolorizing oils, anti-caking agents, flattening agent in paints, catalyst in no-carbon-required paper, and catalyst carrier.

5. Environmental Aspects

Almost all clays are surface mined, so the industry is required to reclaim the disturbed land in most countries. Common practice is to open a cut and then spoil the overburden from the following panels or cuts into the mined out areas. The land is leveled or sloped to meet the governmental requirements and then planted with grasses or trees.